

Tenth and Final Report on the Program
"Viscoelastic Behavior of Polymers at Long Times"
Supported by NASA Grant No. NsG-147-61 at Mellon Institute

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The research program "Viscoelastic Behavior of Polymers at Long Times", as originally conceived, emphasized the investigation of the form of the recoverable creep compliance in the so-called "terminal region" for linear and crosslinked amorphous polymers. Since no instrumentation existed that was capable of accurately measuring recoverable deformation when the total deformation is greatly dominated by viscous flow, it was essential to the program that the appropriate equipment be developed.

Two torsional creep apparatuses have been successfully designed and constructed. In the first¹ the moving element, the rotor, was floated on a low vapor pressure oil. Torques were produced with a pair of wattmeter drive coil units (NASA has applied for a patent on this instrument). With a temperature range extending from 0° to 95°C the instrument proved to be well suited for measurements on crosslinked systems and was extensively used in investigation of the effect of crosslinking on the viscoelastic response of rubbers. [Natural³ and polybutadiene rubbers were studied.] The systematic change in shape of the retardation spectrum with an increasing degree of crosslinking was elucidated and a graphical method for estimating the equilibrium compliance of a rubber was developed. It has been previously claimed that crosslinked natural rubber exhibited Andrade creep (linearity of the compliance with the cube root of time, $t^{1/3}$), but our investigations revealed no such response over a wide range of crosslinking levels. However measurements

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on uncrosslinked samples of natural rubber and polybutadiene did respond at relative long times in accord with the expression $J(t) = J_A + \beta t^{1/3} + t/\eta$, where β and η are characterizing constants and $J(t)$ is the shear creep compliance.

The float torsional creep apparatus, mentioned above, proved to be of limited use for the measurement of linear amorphous polymers because of the small temperature range and the presence of residual torques which were believed to arise from the surface tension of the supporting oil. The second instrument built employed a magnetic suspension for the rotor, thereby eliminating the need for the supporting oil and hence the presence of surface tension forces. Its temperature range was nearly three times as great as the float instrument, -55°C to 225°C . In addition a controlled atmosphere sample chamber was incorporated and a drag cup motor was developed and utilized for producing constant, precisely known torques in lieu of the more cumbersome and limited wattmeter units.

The magnetic suspension instrument has proven highly successful in the measurement of total creep and creep recovery of a wide variety of materials. The performance appears to be limited only by a low level residual torque in the neighborhood of 10^{-3} dyne cm. Many of the results obtained on the crosslinked samples were checked in this apparatus. Among the linear amorphous polymers studied with this apparatus are several fractions of polyvinylacetate, PVAc, with different molecular weights. They have been measured from glassy levels of response out to the region of flow domination. One sample of an ideally atactic polymethylmethacrylate,

PMMA, has been extensively studied over the same range of behavior. Within this range of response these studies have clearly shown that simple temperature reduction is not generally applicable. Previously noted reduction failures for linear amorphous polymers were thought to be the exception and not the rule. Results from a parallel investigation being carried out with the magnetic suspension apparatus on polystyrenes of widely varying molecular weight substantiate this conclusion.

The viscous, viscoelastic and crystallization properties of the glass-forming hydrocarbon 1,3,5 tri- α -naphthyl benzene, TONB, have been studied in detail. Since the mechanical property temperature dependence of all glasses appears to be of the same form near their glass temperatures, it is reasonable to conclude that what we have learned regarding the influence of free volume on the response of TONB will be applicable in analyzing the response of high molecular weight linear amorphous polymers. Because of the nonpolymeric nature of TONB measurement of the viscosity is possible below the glass temperature, T_g . Such measurements are generally precluded for a polymer near and below T_g since the steady state response exists at impossibly long times.

Contrary to the opinion that small molecules have single relaxation times or at least very narrow viscoelastic spectra, we found a retardation spectrum which is over nine logarithmic decades broad. It was a surprise to find the bulk of the recoverable compliance appeared as a terminating Andrade creep; i.e., after a region of time scale where the recoverable deformation is linear with the cube root of time a steady state value is reached. Measurements below T_g indicate that the occupied

volume is insensitive to temperature and viscosity measurements over the temperature range where the rates of crystallization were measurable revealed a temperature dependence which differed from that of the crystallization. For theoretical purposes the two have long been assumed to be identical.

While a number of the originally proposed goals for this program of investigation have been reached we judge the development of the magnetic suspension creep apparatus as the most significant accomplishment during the period of NASA support. It is a tool which can continue to be used to investigate a realm of material behavior which is not accessible by any other means: the measurement of recoverable compliance in a time scale region where total creep is dominated by viscous deformation.

Papers Completed

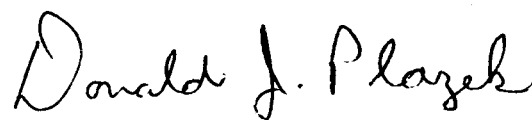
1. "An Instrument for Measuring Torsional Creep and Recovery," D. J. Plazek, Trans. Soc. Rheology 7, 61 (1963).
2. "Crystallization Kinetics of 1,3,5 Tri- α -Naphthyl Benzene," J. H. Magill and D. J. Plazek, Nature 209, 70 (1966).
3. "Effect of Crosslink Density on the Creep Behavior of Natural Rubber Vulcanizates," D. J. Plazek, J. Polymer Sci., in press.
4. "Physical Properties of Aromatic Hydrocarbons. Part I. Viscous and Viscoelastic Behavior of 1,3,5 Tri- α -Naphthyl Benzene," D. J. Plazek and J. H. Magill, J. Chem. Phys., in press.
5. "Physical Properties of Aromatic Hydrocarbons. Part II. Solidification Behavior of 1,3,5 Tri- α -Naphthyl Benzene, J. H. Magill and D. J. Plazek, submitted for publication.

Papers in Preparation

"A Frictionless Torsional Creep Apparatus," D. J. Plazek.

"A Logarithmic Pulse Producer," V. M. O'Rourke.

Extensive investigations have been made on the polymeric systems, polyvinyl acetate, atactic polymethylmethacrylate, and polybutadiene. The data obtained from these investigations will be incorporated in future publications.

A handwritten signature in cursive script that reads "Donald J. Plazek". The signature is written in dark ink and is positioned above the printed name and title.

Donald J. Plazek
Principal Investigator

August 25, 1966